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The measurement of soil CO₂ evolution *in situ*

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With 2 figures

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1. Introduction

It is becoming widely recognized that the belowground portion of terrestrial forested ecosystems accounts for a substantial proportion of net productivity. Accordingly, CO₂ evolution from intact soils has been measured by ecologists and agriculturists to describe the processes that comprise soil metabolism (see reviews by LUNDEGÅRDH 1927, SCHLESINGER 1977, SING & GUPTA 1977). However, measurement remains problematic, despite the availability of numerous techniques. In fact, rates of soil CO₂ evolution vary to a great extent with the particular measurement system used (e.g., MINA 1962, KUCERA & KIRKHAM 1971, MINDERMAN & VULTO 1973, EDWARDS 1974, KANEMASU *et al.* 1974). The lack of a standardized system seriously erodes our ability to compare data collected by different researchers in different localities, and thereby hinders our understanding of this very important measure of ecosystem metabolism.

Two techniques for measuring soil CO₂ evolution *in situ* predominate in the literature; WITKAMP & FRANK (1969) designate them as “static” and “dynamic”. Static techniques utilize a solution of KOH or NaOH to absorb CO₂ that is released from the soil into a closed container. More measurements have probably been conducted with this technique than with any other, although different solution strengths, volumes, chamber sizes, absorption times, and absorption areas have been used, all of which may affect the final value obtained (e.g., KIRITA 1971, GUPTA & SINGH 1977). A new modification of this technique, utilizing solid soda lime as the CO₂ absorbent, is described by EDWARDS (1982), and, because it eliminates use of liquids, may represent a standard methodology for future investigators. EDWARDS also compares soda lime and KOH as absorbents.

With dynamic techniques, an air stream is passed through a chamber placed over the soil, and the amount of CO₂ released into the chamber is monitored with an infrared gas analyzer (IRGA). These techniques are generally considered to be more accurate, but are also much more expensive.

The purpose of our study was to compare two commonly used static techniques with the dynamic technique in order to establish a rationale for selecting a technique and carrying out measurements.

2. Methods

2.0. General remarks

All measurements were taken in a 28-yr-old slash pine (*Pinus elliottii* ENGELM.) plantation in Bradford County, Florida. This site was the 26-yr-old site described by GHOLZ & FISHER (1982). Rainfall in the area averages 1,320 mm/yr, and the average annual temperature is 24 °C (NOAA 1980). The soils are poorly drained Ultic Haplaquods (sandy, siliceous, thermic) with a well-defined litter layer. Stand density averages about 1,100 trees ha⁻¹, and the understory is dominated by saw palmetto [*Serenoa repens* (B.) SMALL] (GHOLZ & FISHER 1982). The stand has not been thinned, fertilized, or burned for at least 10 years.

Measurement chambers were plastic buckets 19 cm tall and 29 cm in diameter. One week prior to measurements, plastic cylinders with the same diameter were randomly placed within the study site. A sharp knife was used to cut through the litter and into the surface soil (A_1 horizon) around each cylinder, to a depth no greater than 5 cm. All living vegetation within the circle was cut off at the soil surface and removed (the litter was not disturbed), and the cylinder was firmly pushed into the soil and left in place. One week later, the cylinders were removed and replaced with the plastic chambers. Preliminary measurements showed that this procedure minimized the increased CO_2 evolution that is often associated with installation of the chambers. Chambers were never placed in the same location twice.

2.1. Static techniques

We used two static techniques to measure soil CO_2 evolution. The first utilized a solution of KOH (hydroxide method), and the second utilized a granular mixture of NaOH and $\text{Ca}(\text{OH})_2$ and CaO (soda lime method). Six replicates of each technique were performed on each measurement date. Our hydroxide method closely followed that of J. EWEL *et al.* (1981).

Twenty-five ml of 1.0 N KOH were placed in an inverted 9 cm diameter Petri dish held above the litter surface on a wire stand. The measuring chamber was immediately placed over this. Every 6 h for a 24 h period the KOH was removed, placed in an air-tight container, and replaced with fresh KOH. Blanks were collected to account for CO_2 absorption during storage and handling. A blank consisted of KOH that was poured into a Petri dish and then immediately back into an air tight sample container.

Following each 24-h experiment the samples were returned to the laboratory and consecutively titrated to the endpoints of phenolphthalein and methyl orange with 0.500 N HCl to determine how much CO_2 they had absorbed. The amount of CO_2 absorbed by the average blank was subtracted from each sample value. The diurnal soil- CO_2 evolution rate in each chamber was determined by averaging the four 6-h samples from that chamber.

A different titration method is often used, in which BaCl_2 is added to each sample to precipitate dissolved carbonates, followed by titration to the phenolphthalein endpoint (BLACK 1965). We titrated 23 samples with both methods and found no significant difference.

Our soda lime method closely followed that described by EDWARDS (1982). We used 60.0 g of 6–12 mesh soda lime inside each 5.2 cm tall, 8.1 cm diameter soil tin. The soda lime was oven dried in the tins at 100 °C for 24 h, weighed to the nearest 0.01 g, and covered tightly. The tins were then taken to the field, uncovered, and placed inside the chambers. After 24 h, the tins were removed, covered, returned to the lab, oven dried for 24 h, and re-weighed. Blanks were collected to account for CO_2 absorption during handling and oven drying; they were opened for just a short time when the samples were put out, and again when the samples were collected.

The amount of CO_2 absorbed by each sample was determined by the mass gain of the sample after subtraction of the mass gained by the average blank. A correction factor of 1.4 was used to compensate for chemical water lost during the drying process (EDWARDS 1982). Used soda lime was replaced after two uses, when CO_2 uptake is less than 12 % of saturation.

2.2. Dynamic technique

We measured soil CO_2 evolution with a flow-through IRGA system similar to that of REINERS (1968) (Fig. 1). Chambers were 30-cm-tall sections of 25 cm i.d. PVC pipes. One end of the pipe was sharpened to enable us to push the cylinders into the soil. Preliminary sampling indicated that data from 6 chambers would generate sample means within 10 % of the mean obtained with 30 chambers 71 % of the time. Chambers were installed one week prior to measurements. Each chamber had intake and exhaust ports located opposite one another, 2–5 cm from the top. These were connected to flow meters with 9 mm i.d. polyethylene tubing. A plexiglass top with a ring of soft latex caulking compound to provide an airtight seal was placed on each chamber approximately 1 h before measurement and was removed immediately after measurement. During daylight hours, the tops were covered with aluminium foil to eliminate sunlight and reduce heat build-up. This design incorporates both the openness and portability that SCHWARTZKOPF (1978) feels are necessary.

Ambient air was supplied to the chambers by a blower and a 1-m³ mixing bag, which was located in the middle of the study plot about 50 cm above the soil. We used flow rates of 1, 4, and 8 l min⁻¹ to determine whether flow rate affected CO_2 evolution. We used a flow rate of 4 l min⁻¹ for the other measurements. Air from each chamber was pumped to a sample jar and then through the IRGA, where its CO_2 concentration was compared with ambient air. Air temperature was monitored with a thermistor probe located inside the mixing bag. The IRGA was calibrated with standard gases prior to each set of diurnal measurements, and was regularly checked by pumping ambient air through both sensors.

At the beginning of each set of diurnal measurements, the system was allowed to equilibrate for 1 h. Each chamber was covered for about 1 h before being monitored. Measurements were taken on each chamber after a steady value was obtained (normally 10 min), and then the chamber was uncovered for about 1 h. Each chamber was therefore monitored for about 10 min every 2 h, 12

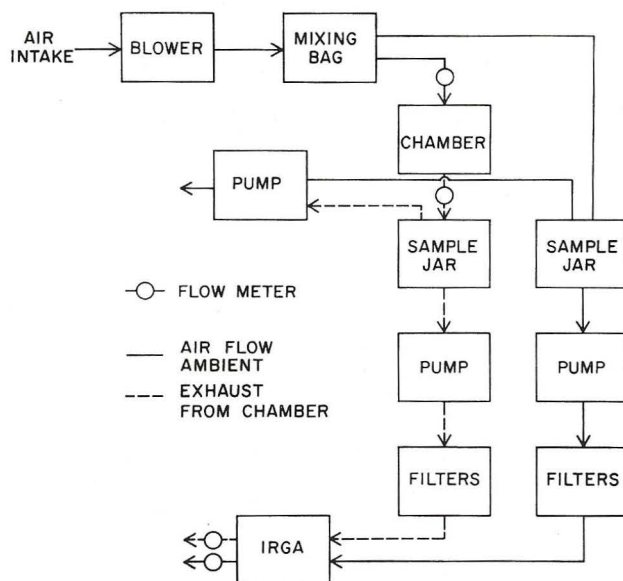


Fig. 1. Flow diagram of IRGA system used to measure soil CO₂ evolution.

times each day. Air temperature within the mixing bag was recorded once during the steady state CO₂ measurement for each chamber. In preliminary measurements, we did not find a significant difference between the temperatures of mixing bag air and air pumped through the IRGA chambers. Temperature data from the mixing bag were used in calculating CO₂ evolution rates. The average daily rate of soil CO₂ evolution inside each chamber was determined by averaging these 12 readings.

2.3. Comparison of techniques

We measured CO₂ evolution rates from the soil once a month for six months using both IRGA (dynamic) and soda lime methods. For 3 months (May, June, and July), we also used the hydroxide method.

In order to test the magnitude of the differences that might exist between the soda lime and IRGA methods, we simulated a constant CO₂ evolution rate by flowing CO₂ (0.5 l min⁻¹) from a standard gas tank through six chambers with soda lime; we used 3 replicates for each of two CO₂ concentrations.

3. Results and discussion

3.1. Comparison of CO₂ evolution rates over 6 months

The dynamic and static techniques used to estimate soil CO₂ evolution over a 6-month period produced similar results when soil temperatures were less than 15 °C (Feb.-March 1983, Fig. 2), but diverged in warmer months. Nevertheless, the two sets of measurements are closely related: a polynomial curve describing the relationship between IRGA data and soda lime data is characterized by a coefficient of determination of 0.87 ($p < 0.05$).

EDWARDS & SOLLINS (1973) also report that static methods were less sensitive than dynamic methods to increased CO₂ evolution at higher temperatures. A wide variety of soil CO₂ evolution data compiled by SCHLESINGER (1977) indicates that results obtained with static techniques are generally lower than those predicted by a regression equation relating latitude to soil CO₂ release, and that dynamic methods often produce values higher than those predicted by the regression equation. Our data suggest that average daily soil respiration rates measured with the IRGA increase with temperature faster than the rates measured with static techniques. We discuss below the limitations involved in interpreting data from each of the three techniques.

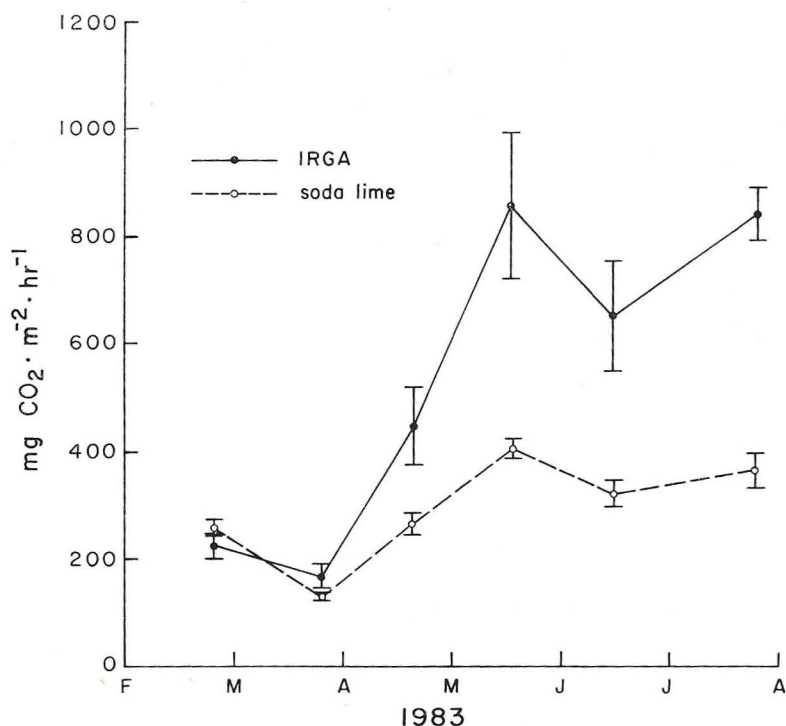


Fig. 2. CO₂ evolution rate ($\bar{x} \pm \text{SE}$) from forest floor, measured by dynamic (IRGA) and static (soda lime) techniques.

Table 1. CO₂ evolution rates (mg CO₂ m⁻² h⁻¹) ($\bar{x} \pm \text{SE}$) measured in an intact forest floor in a 28-year-old pine plantation in 1983

Date	Technique		
	Dynamic	Static	
		Soda Lime	KOH
17 May	854 ± 128	406 ± 25	374 ± 45
16 June	648 ± 93	303 ± 17	357 ± 32
14 July	864 ± 81	372 ± 11	423 ± 12

Note: Three methods of measurement were used.

3.2. Measuring CO₂ evolution with static techniques

There was no difference ($p > 0.05$) between the two types of static absorbents, 1.0 N KOH and soda lime (Table 1). EDWARDS (1982) reports that 0.2 N KOH absorbed significantly less CO₂ than soda lime, but he also cites evidence that higher normalities of KOH and NaOH (which is identical to KOH in its reaction to CO₂) can be either more efficient or less efficient than soda lime. Our data do not provide any additional insight into this controversy.

3.3. Effects of flow rates on CO₂ evolution in dynamic systems

The use of dynamic techniques to measure soil CO₂ evolution is often associated with increased CO₂ evolution rates as flow rate is increased (SCHWARTZKOPF 1978). This flow rate effect has been attributed to flushing of CO₂ from the soil atmosphere (WITKAMP & FRANK

1969) and increased metabolism of soil organisms (SCHWARTZKOPF 1978), perhaps through increased rates of oxygen input. KIMBALL & LEMON (1971) demonstrate that turbulence alone has little effect on soil aeration.

We found no consistent or predictable flow rate effect in a range of chamber turn-over times of 1 to 16 min. CO_2 evolution rates ($\text{mg m}^{-2} \text{h}^{-1} \pm \text{SE}$, $N = 5$, chambers) were 574 ± 170 , 534 ± 212 , and 610 ± 187 at flow rates of 1, 4, and 8 l min^{-1} , respectively. Air speeds within the chambers, measured at the litter surface, ranged from 4.1 cm sec^{-1} at 1 l min^{-1} to 7.1 cm sec^{-1} at 8 l min^{-1} . The range of ambient wind speeds that we measured at the forest floor surface was much wider, even during relatively calm days. We monitored flow rates both at the input and output of each chamber and found (as did KANEMASU *et al.* 1974) that slight suction led to large increases in measured CO_2 release. Carefully balanced inflow and outflow rates are necessary to prevent overestimation of soil CO_2 release.

3.4. Comparison of dynamic technique and both static techniques

Both the absorbents used in the static method measured significantly less CO_2 evolution than the flow-through method (Table 1) ($p < 0.001$), although the coefficients of variation for both static techniques were lower than for the dynamic method. In the simulated CO_2 evolution experiment the mean soda lime mass gain was 3.5 times greater at 860 ppm CO_2 than at 263 ppm. We therefore conclude that seasonal divergence of results from static and dynamic techniques was not due to decreased absorption efficiency at higher respiration rates.

The similarity of results obtained from soda lime and KOH methods in our study does not support EDWARDS & SOLLINS' (1973) hypothesis that lower estimates of CO_2 evolution are due to reduced solubility of CO_2 in KOH at high temperatures. The difference between the flow-through method and the static methods appears to be associated with the movement of air through the chambers. Higher measured CO_2 evolution rates in dynamic *versus* static methods are also reported by WITKAMP (1969), KUCERA & KIRKHAM (1971), and EDWARDS & SOLLINS (1973).

4. Conclusions

Variance associated with spatial heterogeneity limits the accuracy of measurements of soil CO_2 evolution using either technique. Even in the relatively uniform pine plantation where our study was located, it would be necessary to increase sample size to 15 to be within 10% of the mean obtained with 30 samples 90% of the time. This would be operationally difficult with the dynamic system, and, given our requirements for equilibration time and the time necessary for chambers to remain uncovered, would limit assessment of diurnal trends in any single chamber.

In spite of their inability to detect increased rates of CO_2 evolution at higher temperatures, the static techniques remain attractive. The choice between them may be based on ease of access to titration equipment or to a drying oven and an accurate scale. Estimates obtained with the static techniques showed less variation than estimates from the dynamic technique, and could be closely related to them with a polynomial equation. Soda lime or hydroxide data may be useful in increasing intensity of measurements at a given site if they are calibrated to IRGA results at that site.

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Three CO₂ evolution measurement techniques were compared in a 28-year old slash pine plantation (Bradford Co., Florida, U.S.A.). Total forest floor CO₂ evolution was estimated using a dynamic system with CO₂ measured by an infrared gas analyzer (IRGA) system and two static techniques, one using granular soda lime and the other 1.0 N KOH.

CO₂ evolution measured with the IRGA system was not sensitive to variation of flow rates between 1 and 8 l min⁻¹ (4—8 cm sec⁻¹). Coefficients of variation were consistently higher with the dynamic system than with either of the static techniques.

The IRGA method was compared with simultaneous soda lime measurements over a six month period. Although there was no significant difference between winter IRGA and soda lime estimates at low CO₂ evolution rates, the IRGA estimates increased to more than twice the highest soda lime rate during the summer. There was no significant difference between CO₂ evolution rates measured with KOH or soda lime, and we suggest that divergence of dynamic and static methods is related to physical effects of moving air, rather than to the chemistry of the absorbent.

Key words: Carbon dioxide (CO₂), evolution, soil, measurement, technique, infrared gas analysis (IRGA), Potassium hydroxide (KOH), soda lime [NaOH + Ca(OH)₂], adsorbent, comparison.